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(54) **Photosensitive resin base printing material.**

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(73) Proprietor: **Nippon Paint Co., Ltd.**
2-1-2, Oyodokita
Oyodo-ku
Osaka-shi Osaka-fu(JP)

(72) Inventor: **Umeda, Yasushi**
1922-156, Noji-cho
Kusatsu-shi Shiga-ken(JP)

(74) Representative: **Smulders, Theodorus A.H.J., Ir. et al**
Vereenigde Octrooibureaux
Nieuwe Parklaan 97
NL-2587 BN 's-Gravenhage (NL)

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Description

The present invention relates to a photosensitive resin base printing material and more specifically, it concerns a photosensitive resin base printing material characterizing by providing a slip layer of a high molecular substance containing a dyestuff on a photosensitive resin layer, which is excellent in resolution and can be easily handled and visually inspected in the preparation of a printing plate.

In various relief printing areas including newspaper printing, flexographic printing and the like, a photosensitive resin base printing material has been widely used. Such material is usually constructed as a laminate comprising, in successive order, a support, a photosensitive layer consisting essentially of a developer soluble, high molecular binder, a polymerizable unsaturated monomer or monomers and a photo-initiator, a slip layer of a high molecular substance for the purpose of improving a close contact of the photosensitive resin layer to an original, a releasing layer and a protective film or sheet. On the use of such material, the protective film or sheet and the releasing layer are peeled off to expose the slip layer of the laminate. An original is then placed on said slip layer and exposed to an actinic radiation for a desired time to effect photo-curing (or setting) of the exposed resin layer.

The exposed material is then treated with a developer to remove the unexposed, uncured photosensitive resin and the slip layer to obtain a printing plate having a relief exactly copying the image in the original.

Therefore, from a standview of light penetration, it is preferred that the said photosensitive layer is as clear as possible, and, in fact, many of the commercialized printing materials do bear a transparent photosensitive resin layer.

Light goes right on in essence and however, it is well known that when a light beam passes through a medium with a certain thickness, there often occurs irregular reflection or refraction of the light depending on the nature of said medium.

In the preparation of a relief printing plate by using a photosensitive resin base printing material, such irregular reflection or refraction of an incident light is believed to be important for the formation of shoulder of the relief image.

However, too excessive amounts of irregular reflection or refraction are undesirable because it would cause photo-curing, in certain degree, at the unexposed area of the photosensitive layer (the so-called fogging phenomenon), and hence, a deficient dissolving of the photosensitive layer at the unexposed area, in a development stage.

More concretely speaking, at the time when a half-tone negative with various sizes of dots is closely contacted as an original with a transparent photosensitive resin layer and exposed to a light, there are indeed no particular problems at the portion of said photosensitive resin layer where it is contacted with negative dots having comparatively smaller dot-area (the so-called high-light area of letterpress), but at the portion where the photosensitive resin layer is contacted with negative dots having comparatively larger dot-area (the so-called shadow area of letterpress), there arises the so-called fogging phenomenon, thereby resulting loose shoulder under the influence of irregular reflection of incident light and reflected light from a support. As a consequence, a shallow depth image is formed at the shadow area of the printing plate and a solid printing is resulted therewith.

Attempts have been, therefore, made to provide an antihalation layer containing a pigment or dyestuff which will absorb visible or ultraviolet rays used in an exposure stage, between a photosensitive resin layer and a support, thereby absorbing the reflected light from the support and reducing the undesired influence of the reflected light toward shadow area. However, in that case, the desired amounts of reflected light for high-light area are likewise absorbed and therefore, there often arises the case wherein high-light area, fine letter or fine dot area are exposed deficiently. To compensate the same, a longer time exposure is required.

Moreover, it is essential that a non-diffusing coloring matter should be selected. This is because, if the coloring matter is of diffusible nature, there is a tendency that the coloring matter used would migrate into a lower portion of the photosensitive layer through diffusion, whereby the reflected light desired for photo-curing of resin at that portion is objectionably absorbed. Thus, there occurs a side-edging of the image at high-light area, fine letter or fine dot area and in an extreme case, undesired falling off of the relief image.

In another attempts, such coloring matters are directly added to and uniformly kneaded with a photosensitive resin composition to be used for the preparation of photosensitive layer. However, in this case, an incident light is inevitably absorbed by the photosensitive layer itself in regular succession as it goes through said layer.

Therefore, there is a severe side-edging of the relief image at the high-light area and the like and falling off of the desired image. Even if a long time of exposure is adopted, there are various troubles as fogging and the like at the shadow area, in return.

Thus, a photosensitive resin base printing material capable of resulting high quality images both in shadow area where it is easily affected by irregular reflection of incident light and reflected light from a support at a comparatively upper portion of

a photosensitive layer and in high-light area where it is easily affected by a transmitted light and reflected light from a support at a comparatively lower portion of the photosensitive layer has never been found yet.

It is, therefore, an object of the present invention to privide a relief printing material capable of resulting in high quality images both in high-light and shadow areas, through conventional processes of photo-exposure and development. An additional object of the invention is to provide a relief printing material having an improved resolution.

The above-mentioned and other objects of the invention can be obtained by a photosensitive resin base material in the form of a laminate including, in successive order, a support, a photosensitive resin layer, and a slip layer of a high molecular weight substance which contains a dyestuff, said photosensitive material being characterized in that

- it is a relief printing plate which moreover includes a protective sheet or film on top of the slip layer and optionally also a releasing layer between the protective sheet or film and the slip layer,
- the photosensitive layer comprises a high molecular weight binder, at least one polymerizable unsaturated monomer and a photo-initiator,
- the high molecular weight substance of the slip layer is a substance which is soluble or swellable in a developer and is selected from cellulose resins and at least partially saponified vinyl acetate polymers,
- the dyestuff contained in the slip layer is an anthraquinone dyestuff which can be photobleached by actinic radiation in the visible to ultraviolet region, said dyestuff being present in an amount of from 0.01 to 20% by weight on the total weight of the high molecular weight substance, and
- the slip layer has a dry film thickness of from 0.5 to 20 μm.

EP-A-0 110 165 discloses a photosensitive material in the form of a laminate which comprises a support, a photosensitive resin layer and a contrast enhancing layer. The material is intended for use in producing a mask for the manufacturing of integrated circuits. In order to obtain a better image definition for the purpose intended the contrast enhancing layer contains a yellow colored nitrone dyestuff, which is easily bleached on prolonged exposure.

From FR-A-2 122 578 a photosensitive resin base material is known that is intended for use in producing masks for the manufacturing of printed circuits. The photosensitive material comprises, in successive order, a protective sheet, a thin photosensitive resin layer, a layer of a soluble polymer containing a dyestuff, and a support sheet. The dyestuffs described therein are different from the anthraquinone dyestuffs used according to the present invention. Photo-exposure is carried out through the protective sheet, whereas the photosensitive material according to the present invention is photo-exposed through the dyestuff containing slip layer after the protective sheet has been removed.

In this invention, as a support, the following may be satisfactorily and advantageously used in a sheet or film form:
a metal such as aluminium, zinc or iron;
a plastic material such as polyethylene terephthalate, polyethylene, polymethyl methacrylate, Nylon, cellulose acetate, polypropylene, polycarbonate or polyvinyl chloride; a natural or synthetic rubber, a rubber foam (e.g. urethane foam, butadiene foam); a glass material; and any combination or laminate thereof. If desired, the support surface may be pretreated by etching, anodizing or corona discharge, or applied with an adhesive layer and/or an antihalation layer beforehand.

On this support, is usually placed a photosensitive layer consisting essentially of a high molecular binder, a polymerizable unsaturated monomer or monomers, and a photo-initiator.

As the binder, there may be used any high molecular material which is compatible with the polymerizable unsaturated monomer and the photo-initiator and combine a composition for the photosensitive layer onto the support.

Examples of such binder are crystalline 1,2-polybutadiene, styrene-butadiene-styrene copolymer, styrene-isoprene-styrene copolymer, nitrile butadiene resin, polyamide resin which is soluble in a lower alcohol or water, polyurethane resin, polyester resin and polyvinyl alcohol.

Among them, particularly preferred members are crystalline 1,2-polybutadiene, styrene-butadiene-styrene copolymer, and styrene-isoprene-styrene copolymer, because they are easily formed into sheets at a relatively lower temperature without the risk of causing thermal polymerization of the polymerizable unsaturated monomers used.

The polymerizable unsaturated monomers may be any members customarily used in this type of photosensitive resin layer as, for example, 2-ethyl hexyl acrylate, 2-ethyl hexyl methacrylate, octyl acrylate, octyl methacrylate, lauryl acrylate, lauryl methacryalte, stearyl acrylate, stearyl methacrylate, trimethylolpropane triacrylate, trimethylolpropane trimethacrylate, trimethylolethane triacrylate, trimethylolethane trimethacryalte, ethylene glycol acrylate, ethylene glycol methacrylate, triethylene glycol diacrylate, triethylen glycol dimethacryatle, β-hydroxyethyl acrylate, β-hydroxyethyl methacrylate, β-hydroxypropyl acrylate, β-hydrox-

ypropyl methacrylate, acrylamide, methacrylamide and N,N'-methylenebisacrylamide.

It is, of course, possible to use other unsaturated compounds than the abovementioned monomers, provided they have properties of being polymerized with the help of photo-activated photo-initiator and being compatible with the binder material used.

The third component of photo-initiator may be any compound capable of being activated by a radiation and initiating the polymerization of said monomer(s). Examples of such compounds are benzoin, benzoin alkyl ether, benzyl, acetophenone, 2,2-dimethoxy 2-phenyl acetophenone, benzyl anthraquinone, 2-methyl anthraquinone, 2-t-butyl anthraquinone, p-dinitrobenzene, 2-chloro-4-nitroaniline, 9-anthranyl aldehyde, benzophenone and 1,2-naphthoquinone, 4-naphthoquinone. Among them, particular preference is given to benzoin, benzoin alkyl ether, and 2,2-dimethoxy-2-phenyl acetophenone, because they are stable even at the molding temperature of the photosensitive resin layer composition.

The photosesitive resin layer of this invention consists essentially of the above-mentioned polymeric binder, polymerizable unsaturated monomer(s) and photo-initiator, and however, other additives as thermal polymerization inhibitor (e.g. hydroquinone, p-methoxy phenol, t-butyl catechol, 2,6-di-t-butyl cresol) and plasticizer may be added if desired.

The photosensitive resin layer is advantageously formed directly on the support by, for example, an extrusion molding of a photosensitive resin composition containing the abovesaid components. However, it is, of course, possible to make the photosensitive resin sheet or film beforehand, contact the same, with or without an intervenning adhesive layer, with a support and effect a contact-bonding of thus formed laminate.

The bonding of said photosensitive layer with the support may be effected by any conventional means as heat pressing, casting, solution casting, lamination or extrusion molding.

A slip layer of a high molecular substance as defined below is positioned between the photosensitive layer and the releasing layer hereinunder stated or, in the absence of such releasing layer, a protective layer hereinunder stated, to furnish a smooth and non-tacky surface and secure a close contact of the photosensitive layer with an original at the exposure stage. This layer is required to be soluble or swellable in water or alcohol or other solvents used for the development of the photosensitive resin layer.

In this invention, an anthraquinone dyestuff is included in a specified amount in this slip layer, which is the most characteristic feature of this invention.

The presence of such dyestuff in a relatively thin slip layer of 0.5 to 20 µm thickness, preferably 0.5 to 10 µm thickness, is effective for controlling the amounts of incident light and reflected light from the support at a relatively upper portion of the photosensitive layer and giving a better quality image at a shadow area of the printing plate. Even if a part of said dyestuff migrates into an upper part of the photosensitive layer through diffusion, the most parts of said photosensitive layer and especially the lower part thereof are maintained in substantially clear state and therefore, there is no undesirable decrease in light volume of penetrating light and good quality image can be secured even at a high-light area of the printing plate.

The anthraquinone dyestuff used has photo-bleaching properties when exposed to actinic radiation in the visible to ultraviolet region.

More specifically, the following anthraquinone dyestuffs having the above-mentioned properties and having a cyan color may be employed:
C.I. disperse blue 26 (color index 63305), C.I. Solvent blue 11 (color index 61525), C.I. Solvent blue 36 and C.I. Solvent blue 93.

These dyestuffs are soluble in water, alcohol or organic solvents and are employed each singularly or in combination form.

Employment of such photo-bleaching dyestuff affords the benefit that since the dyestuffs contained in an exposed area are rapidly photo-bleached, a far more reliable light penetration can be realized at the high-light area and a far better control of image quality in both high-light and shadow areas can be attained.

When an anthraquinone dyestuff which has the properties of being photo-bleached by visual or ultraviolet rays and regaining or re-developing color after oxidation in air, is used in said slip layer, the formed relief image can be more easily visualized by naked eyes. The high molecular substance to be used in said slip layer must be soluble or swellable in a developer. This must also be compatible with said dyestuff and must be a binder and combine the layer onto the photosensitive layer. From these standviews, the high molecular substance is selected from cellulose resins and at least partially saponified vinyl acetate polymers. Specific examples are as follows:

(1) Vinyl acetate polymers (homopolymers and copolymers) which are at least partially saponified. Examples are polyvinyl alcohol, 50% saponified polyvinyl acetate, vinyl acetate-vinyl chloride-maleic acid copolymer, vinyl acetate-ethylene copolymer, vinyl acetate-acrylic acid copolymer and a tripolymer of vinyl butyral, vinyl acetate and vinyl alcohol The content of the vinyl alcohol units is preferred to be 5 to 95

mole % based on the total amount of the monomeric units.

(2) Cellulose resins such as methyl cellulose, ethyl cellulose, cellulose acetate butyrate, nitrocellulose, cellulose phthalate, hydroxymethyl cellulose, hydroxypropyl cellulose and hydroxypropylmethyl cellulose phthalate

Among them, particular preference is given to methyl cellulose (e.g. Metrose, trademark of Shinetsu Kagaku), ethyl cellulose (e.g. Ethocellu, trademark of Dow Chemical), polyvinylalcohols (e.g. KH-20, KH-17, trademarks of Nihon Gosei Kagaku), cellulose acetate butyrate (e.g. CAB 381, trademark of Eastman Kodak Co.) and carboxymethyl cellulose (e.g. Sanrose, trademark of Sanyo Kokusaku Pulp), because of giving a smooth, non-tacky surface on said slip layer.

The abovesaid high molecular substance and the anthraquinone dyestuff may be admixed in an appropriate proportion depending on the use.

Usually, to 100 parts by weight of the high molecular substance, 0.01 to 20 parts by weight, more preferably 0.1 to 10 parts by weight, of the dyestuff are employed. When the amount of the dyestuff is less than the said lower limit, the coloring becomes weak resulting in the decrease in contrast between an exposed area and an unexposed area.

When the amount is larger than the said upper limit, a long time exposure is required for obtaining a better quality image at the high-light area and for the required photo-bleaching reaction to reduce the practical value.

In addition to said essential components, there may be incorporated in the slip layer any additives such as a plasticizer, a dispersing agent and a sensitizing agent, for various purposes as improvement in compatibility between the dyestuff and the high molecular substance, acceleration of photobleaching reaction, improvement in various physico-chemical properties of the formed coating.

In preparing a slip layer on the photosensitive layer, the aforesaid various components are dissolved in an appropriate solvent and thus obtained solution is directly applied on the photosensitive layer.

Alternatively, the said solution is coated on a silicon releasing layer provided on a sheet or film form of protective layer or directly on a protective sheet or film, to make the desired slip layer and thus formed laminate is bonded onto the photosensitive resin layer provided on a support by conventional means.

As the solvent, any of the medium capable of dissolving the high molecular substance, dyestuff and other additives may be satisfactorily used, including water, alcohols (e.g. methanol, ethanol, propanol), ketones (e.g. acetone, methyl ethyl ketone), aromatic hydrocarbons (e.g. benzene, toluene, xylene) and combination thereof.

The solid content of said solution is usually from 1 to 60 % by weight, preferably from 5 to 40 % by weight.

This is because if the solid concentration is less than 1 %, the solution viscosity will become too low and it is difficult to obtain a coating with the desired thickness and if the solid concentration exceeds over the upper limit of 60 % by weight, it is quite difficult to obtain the desired clear solution.

The application of thus obtained solution may be effected by any conventional means as dipping, brushing, spraying, roll-coating, curtain coating or bar coater coating.

After applying the solution, it is air-dried, vacuum dried or hot-air dried to obtain the colored slip layer.

The dry film thickness of said layer is from 0.5 to 20 μm and preferably from 0.5 to 5 μm. If the slip layer thickness is less than 0.5 μm, the dyestuff concentration is too low to have the desired effects of the invention and if it exceeds over the upper limit of 20 μm, there is a tendency that the photosensitivity of the underlying resin layer will be lowered and turbidity will be appeared at the exposed area.

The protective film or sheet may be made of any plastic materials (e.g. polyester, polycarbonate, polyacrylate or polypropylene), whose surface may preferably be roughened by chemical etching or physical polishing (e.g. sandblast) to a surface roughness of 5 μm or less.

The thickness of the protective film or sheet may be varied in a considerable range, but it is preferred to be from about 10 to 300 μm.

In order to assure the separation of the protective film or sheet from the slip layer, a releasing layer should preferably be provided therebetween.

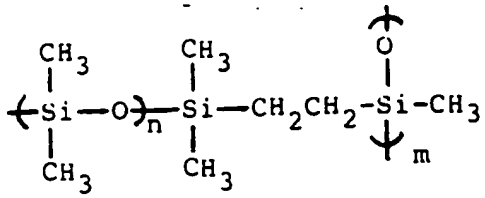
Such releasing layer may be provided by treating said roughened surface of the protective film with a silicone resin so as to give a dry-thickness of about 0.1 to 0.5 μm.

If the releasing layer is not provided, the complete and easy separation of the protective film or sheet from the slip layer is rather difficult to do even if the photosensitive resin layer has a great tackiness.

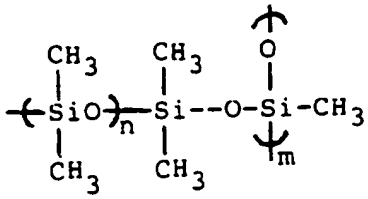
Therefore, employment of such releasing layer, though it is not essential in the present invention, is highly recommended.

In this case, the aforesaid slip layer may be advantageously formed on the releasing layer and thus formed laminate is bonded to the photosensitive resin layer.

As the silicone resin, there are known two types of resins, i.e. (A) the addition curing type resin having the formula:



and (B) the condensation curing type resin having the formula:



Examples of the commercially available silicone resins are Toray silicone paper coating agents of addition type "SD 7226" (catalyst "SRX 212" and of condensation type "SRX 244" (catalyst "SRX 242 AC").

The invention can never be limitted to any specific method used for the production of said laminated, relief printing material. However, the photosensitive resin layer provided on a support and the colored slip layer provide, with or without intervention of a releasing layer, on a protective film or sheet are preferably brought into close contact and bonded by a conventional combining means as heat pressing, laminating or extrusion molding.

On the use of thus formed relief printing material, the protective film or sheet is eliminated, with or without the releasing layer, so that the colored slip layer remains on the surface of the photosensitive resin layer. Then, an original is placed on said slip layer and the combined sandwich is exposed to light for a desired period of time. Treatment of the exposed material with a developer, preferably while brushing, accomplishes development and affords a printing plate having an excellent relief exactly copying the image in the original.

For development of such photosensitive resin base relief printing material, there may be used any solvent system comprising, for example, as the major solvent water, an alkaline aqueous solution, an alcohol, a chlorinated hydrocarbon (e.g. perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride), an aromatic hydrocarbon (e.g. toluene, xylene), a ketone (e.g. methyl ethyl ketone, methyl isobutyl ketone), a cellosolve acetate or any combination of the same.

However, an optimum solvent system may advantageously be selected depending on the high molecular binder used in the photosensitive resin layer.

Since the photosensitive resin base relief printing material of the invention has the colored slip layer on the surface of the photosensitive resin layer, the tackiness of the photosensitive resin layer does not cause any problems.

Further, the favorable lubricity of the slip layer makes easy the operation to bring an original into close contact with the surface of the photosensitive resin layer.

Besides, the slip layer is readily eliminated on treatment with water, alcohol, organic solvent or combination thereof for development and therefore does not afford any unfavorable influence on the printing characteristics of the printing plate obtained from the present printing material.

Furthermore, an anthraquinone dyestuff is included in an effective amount in said slip layer and therefore, it will absorb a quantity of incident light and reflected light from a support at an upper portion of the photosensitive resin layer, but can never give any undesired effect on the penetrating light at the lower portion of the photosensitive resin layer.

Therefore, an optimum condition for the exposure of both upper and lower portions of the resin layer can be established therewith, and better quality images can be obtained in both high-light and shadow areas. Resolution of a printing material is thus improved in great extent. Even if the anthraquinone dyestuff in the slip layer should migrate into the photosensitive resin layer, it always remains at a considerable concentration at an upper portion of the resin layer, and therefore, the aforesaid benefical effects can be likewise obtained.

The invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and percentages are by weight.

Example 1

In this example, a photosensitive resin sheet consisting of 66.00 wt% sindiotactic 1,2-polybutadiene, 27.19 wt% tetrahydro-dioctylphthalate, 5.35 wt% neopentylglycoldimethacrylate, 0.70 wt% benzyl-dimethylketal, 0.52 wt% 2,6-di-t-butyl-p-cresol and 0.04 wt% hydroquinone monomethylether was used.

Onto one surface of said photosensitive resin sheet of 5 mm thickness, a polyester sheet was provided as a supporting material.

Separately, on a protective polyester film whose surfaces have previously been chemically etched (100 µm in thickness and 3.0 µm in aver-

age roughness), Toray silicone SRX 244 (solvent type silicone resin, trademark of Toyo Rayon, with SRX 242 AC catalyst) was applied by a doctor blade so as to give a releasing layer of 0.5 μm in thickness. After being allowed to stand at a room temperature for 24 hours, a 5 % by weight solution of a mixture of 100 parts of ethyl cellulose (45% ethoxy content, medium type, Dow Chem.) and 0.2 part of Sumiplast blue-G (Trademark of Sumitomo Chem. Co., C.I. Solvent blue 11, color index 61525) in an isopropyl alcohol / toluene mixed solvent was applied onto the releasing layer by means of a bar coater to make a colored slip layer of 3 μm thickness and dried.

Then, the aforesaid photosensitive resin sheet backed with the supporting material was heated in a hot wind drying furnace at 60 • C for 2 minutes, and the colored slip layer formed on the protective polyester film with intervention of the releasing layer was brought into contact with the heated photosensitive resin sheet to combined them together. Thus prepared laminate was placed on a cooling plate having a surface temperature of 16 • C for 10 minutes to give a photosensitive resin base printing material, in which a colored slip layer was provided on one surface of the photosensitive resin layer and said slip layer was protected by a protective polyester film.

After removing the protective polyester film from thus obtained laminated product, there was obtained a photosensitive material having a photosensitive resin layer whose surface was covered by a non-tacky, dyestuff-containing ethyl cellulose film layer (3 μm thickness and 2.4 μm maximum surface roughness) (the so-called slip layer).

An original was placed on said slip layer of the photosensitive material. This placement was easily done and the original was retained at a good contact state.

Then, a ultraviolet ray lamp was irradiated onto the photosensitive resin layer through the original and the colored slip layer for 10 minutes, and the original was taken off. This taken off was easily done without damaging the original as well as the photosensitive material. The exposed area of said material was clear by a photo-bleaching of the dyestuff contained and the unexposed area was blue color. Thus, the original image pattern was visually obserbed by naked eyes in full.

The thus exposed material was then washed with a mixture of isopropanol and 1,1,1-trichloroethane (1 : 3 by volume) under brushing for development and dried in a drying furnace at 50 • C for 20 minutes to give a printing plate having a relief exactly copying the image in the original. The exposed area was blue and the shoulder shape of the relief image was excellent.

Example 2

Onto one surface of the photosensitive resin sheet of 3 mm thickness having the same composition with that of Example 1, a polyester sheet was provided as a supporting material.

Separately, on a protective polyester film whose surfaces were not chemically etched (100 μm in thickness), Toray silicone SRX 244 was applied by a doctor blade so as to give a releasing layer of 0.5 μm in thickness. After being allowed to stand at a room temperature for 24 hours, a 5 % by weight solution of a mixture of 100 parts of a tripolymer of vinyl butyral, vinyl acetate and vinyl alcohol (butyrallization 65 ± 2 mole %; number average molecular weight 1000 to 2000) and 0.3 part of Sumiplast blue G in isopropyl alcohol was applied onto the releasing layer by a bar coater to give a colored slip layer of 3 μm thickness and dried.

Then, the abovesaid two were laminated together as in Example 1 to obtain a photosensitive resin base printing material (A).

From the printing material (A), the polyester sheet used as a supporting material was peeled out and the exposed surface of the photosensitive resin layer was contact-bonded to a rubber base plate (Kureha A, trademark of Kureha Kagaku, 2.8 mm thickness) wetted with 1,1,1-trichloroethane. Thus obtained laminate was allowed to stand for 1 hour to prepare a photosensitive resin base printing material (B) having a photosensitive resin layer whose one surface was coated by a non-tacky, blue colored slip layer and the other surface was backed by a rubber base plate of 2.8 mm in thickness.

They were then, after peeling off the respective protective polyester film, exposed to ultraviolet rays through original and developed as in Example 1. However, in this Example, 1,1,1-trichloroethane was used as a developer and the drying operation was conducted in a drying furnace at 45 • C for 20 minutes.

Blue-colored, relief image exactly copying the image in the original and having excellent shoulder shape was obtained in either case.

Example 3

From the photosensitive resin base printing material (A) obtained in Example 2, the polyester sheet used as a supporting material was peeled off.

Separately, onto a closed cell type urethane foam bonded to a polyester film (3 mm thickness, 0.32 density, 115 % elongation, 38 % impact resilience, 4.6 % compression set), was applied chloroprene rubber adhesives and dried to make an adhesive layer of 20 to 30 μm in thickness.

The exposed surface of the photosensitive resin layer was contact-bonded with said adhesive layer to obtain a photosensitive resin base printing material (C).

Thus obtained material (C) was treated in the same way as in Example 2 and an excellent printing plate having blue colored relief image and excellent shoulder shape was obtained.

This plate was set in a flexographic printing machine and used for printing of card boards.

The print was excellent, having no marginal zone and having good image in shadow area as well as in high light area.

Example 4

The same procedures as stated in Example 3 were repeated, except for substituting a closed cell type chloroprene foam bonded to a polyester film (4 mm thickness, 0.19 density, 168% elongation, 32% impact resilience, 25.5% compression set) for the urethane foam bonded to polyester film.

Very similar results as given in Example 3 were obtained.

Claims

1. A photosensitive resin base material in the form of a laminate including, in successive order, a support, a photosensitive resin layer, and a slip layer of a high molecular weight substance which contains a dyestuff, characterized in that
   - the photosensitive material is a relief printing plate which moreover includes a protective sheet or film on top of the slip layer and optionally also a releasing layer between the protective sheet or film and the slip layer,
   - the photosensitive layer comprises a high molecular weight binder, at least one polymerizable unsaturated monomer and a photo-initiator,
   - the high molecular weight substance of the slip layer is a substance which is soluble or swellable in a developer and is selected from cellulose resins and at least partially saponified vinyl acetate polymers,
   - the dyestuff contained in the slip layer is an anthraquinone dyestuff which can be photo-bleached by actinic radiation in the visible to ultraviolet region, said dyestuff being present in an amount of from 0.01 to 20% by weight on the total weight of the high molecular weight substance, and
   - the slip layer has a dry film thickness of from 0.5 to 20 μm.

2. A photosensitive material according to claim 1, characterized in that the high molecular weight substance of the slip layer is soluble or swellable in water, alcohol, organic solvent or a combination thereof.

3. A photosensitive material according to claim 1 or 2, characterized in that the support is a metal plate, a plastic plate, a natural or synthetic rubber plate, a synthetic rubber foam plate, a glass plate or a laminate of either combination thereof.

4. A photosensitive material according to any of claims 1-3, characterized in that the protective sheet or film is a plastic sheet or film having a surface roughness of 5 μm or less.

5. A photosensitive material according to any of claims 1-4, characterized in that the releasing layer is a silicone type releasing layer.

6. A photosensitive material according to any of claims 1-5, characterized in that the releasing layer has a thickness of from 0.1 to 0.5 μm.

7. A method for preparing a relief printing plate, characterized in that the protective sheet or film together with the releasing layer, when present, are removed from a photosensitive material according to any of claims 1-6, an original is placed in contact with the slip layer, the photosensitive resin layer is exposed to visible or ultraviolet rays to effect photocuring of the photosensitive resin layer at the exposed areas, the original is removed, the exposed photosensitive resin layer is developed with a developer which at the same time eliminates the slip layer, and the thus developed relief image is dried.

Patentansprüche

1. Photosensitives Material auf Harzbasis in Form eines Laminates, der Reihe nach enthaltend einen Träger, eine photosensitive Harzschicht und eine Kontaktschicht aus einer Substanz mit einem hohen Molekulargewicht, die einen Farbstoff enthält, dadurch gekennzeichnet, daß
   - das photosensitive Material eine Reliefdruckplatte ist, die weiterhin eine Schutzfolie oder einen Schutzfilm auf der Kontaktschicht und gegebenenfalls weiterhin eine Abziehschicht zwischen der Schutzschicht oder dem Schutzfilm und der Kontaktschicht enthält,
   - die photosensitive Schicht ein Bindemittel mit einem hohen Molekulargewicht,

wenigstens ein polymerisierbares, ungesättigtes Monomer und einen Photoinitiator umfaßt,

- die Substanz mit hohem Molekulargewicht der Kontaktschicht eine Substanz ist, die in einem Entwickler löslich oder quellbar ist und ausgewählt ist aus Cellulose-Harzen und wenigstens teilweise verseiften Vinylacetatpolymeren,
- der in der Kontaktschicht enthaltene Farbstoff ein Anthrachinon-Farbstoff ist, der durch aktinische Strahlung im sichtbaren bis ultravioletten Bereich photo-gebleicht werden kann, wobei der Farbstoff in einer Menge von 0,01 bis 20 Gew.-% des Gesamtgewichtes der Substanz mit hohem Molekulargewicht vorliegt, und
- die Dicke der Kontaktschicht als Trokkenfilm 0,5 bis 20 µm beträgt.

2. Photosensitives Material gemäß Anspruch 1, dadurch gekennzeichnet, daß die Substanz mit hohem Molekulargewicht der Kontaktschicht in Wasser, einem Alkohol, einem organischen Lösungsmittel oder einer Kombination davon löslich oder quellbar ist.

3. Photosensitives Material gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Träger eine Metallplatte, eine Kunststoffplatte, eine Platte aus natürlichem oder synthetischem Gummi, eine Platte aus synthetischem Gummischaum, eine Glasplatte oder ein Laminat aus einer Kombination davon ist.

4. Photosensitives Material gemäß einem der Ansprüche 1 - 3, dadurch gekennzeichnet, daß die Schutzfolie oder der Schutzfilm eine Kunststoffolie oder ein Kunststoffilm mit einer Oberflächenrauhigkeit von 5 µm oder weniger ist.

5. Photosensitives Material gemäß einem der Ansprüche 1 - 4, dadurch gekennzeichnet, daß die Abziehschicht eine Abziehschicht vom Silikon-Typ ist.

6. Photosensitives Material gemäß einem der Ansprüche 1 - 5, dadurch gekennzeichnet, daß die Abziehschicht eine Dicke von 0,1 bis 0,5 µm besitzt.

7. Verfahren zur Herstellung einer Reliefdruckplatte, dadurch gekennzeichnet, daß die Schutzfolie oder der Schutzfilm zusammen mit der Abziehschicht, falls vorhanden, von einem photosensitiven Material gemäß einem der Ansprüche 1 - 6 entfernt werden, ein Original in Kontakt mit der Kontaktschicht gebracht wird, die Schicht aus photosensitivem Harz sichtbaren oder ultravioletten Strahlen ausgesetzt wird, um eine Photohärtung der Schicht aus dem photosensitiven Harz an den belichteten Bereichen zu bewirken, das Original entfernt wird, die belichtete Schicht aus photosensitivem Harz mit einem Entwickler entwickelt wird, der gleichzeitig die Kontaktschicht beseitigt, und das so entwickelte Reliefdruckbild getrocknet wird.

Revendications

1. Matériau d'impression à base de résine photosensible sous la forme d'un stratifié comprenant, successivement, un support, une couche de résine photosensible et une couche de glissement d'une substance de haut poids moléculaire qui contient un colorant, ledit matériau photosensible étant caractérisé en ce que
   - le matériau photosensible est une plaque d'impression en relief qui comprend en outre une feuille ou un film de protection par-dessus la couche de glissement et, facultativement aussi, une couche séparable entre la feuille ou le film de protection et la couche de glissement,
   - la couche photosensible comprend un liant de haut poids moléculaire, au moins un monomère insaturé polymérisable et un photoinitiateur,
   - la substance de haut poids moléculaire de la couche de glissement est une substance qui est soluble ou gonflable dans un révélateur et elle est choisie parmi les résines cellulosiques et les polymères d'acétate de vinyle au moins partiellement saponifiés,
   - le colorant contenu dans la couche de glissement est un colorant anthraquinonique qui peut être photoblanchi par un rayonnement actinique dans la région du visible à l'ultraviolet, ledit colorant étant présent en quantité de 0,01 à 20 % en poids par rapport au poids total de la substance de haut poids moléculaire et
   - la couche de glissement a une épaisseur de film à sec de 0,5 à 20 µm.

2. Matériau photosensible selon la revendication 1, caractérisé en ce que la substance de haut poids moléculaire de la couche de glissement est soluble ou gonflable dans l'eau, l'alcool, un solvant organique ou une de leurs combinaisons.

3. Matériau phososensible selon la revendication 1 ou 2, caractérisé en ce que le support est

une plaque métallique, une plaque en matière plastique, une plaque en caoutchouc naturel ou synthétique, une plaque de mousse de caoutchouc synthétique, une plaque de verte ou un stratifié de l'une quelconque de leurs combinaisons.

4. Matériau photosensible selon l'une quelconque des revendications 1 à 3, caractérisé en ce que la feuille ou le film de protection est une feuille ou un film de matière plastique ayant une rugosité de surface de 5 µm ou moins.

5. Matériau photosensible selon l'une quelconque des revendications 1 à 4, caractérisé en ce que la couche séparable est une couche séparable du type silicone.

6. Matériau photosensible selon l'une quelconque des revendications 1 à 5, caractérisé en ce que la couche séparable a une épaisseur de 0,1 à 0,5 µm.

7. Procédé de fabrication d'une plaque d'impression en relief, caractérisé en ce que la feuille ou le film de protection avec, le cas échéant, la couche séparable, sont séparés du matériau photosensible selon l'une quelconque des revendications 1 à 6, un original est placé en contact avec la couche de glissement, la couche de résine photosensible est exposée à un rayonnement visible ou ultraviolet pour effectuer la photoréticulation de la couche de résine photosensible dans les zones exposées, l'original est retiré, la couche de résine photosensible exposée est développée avec un révélateur qui élimine en même temps la couche de glissement et l'image en relief ainsi développée est séchée.